

EFFECT OF OXIDATIVE WEATHERING ON ALIPHATIC STRUCTURE OF COAL

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ABSTRACT

Oxidative weathering of coal affects its structure and properties, and as a result, its utilization. For example, weathering adversely affects liquefaction yield, cokability, calorific value, and beneficiation. However, little is known about the chemistry of coal weathering. This paper discusses the effect of weathering on the aliphatic crosslinks that connect the aromatic-hydroaromatic units in coal. These crosslinks play a significant role in coal liquefaction and weathering alters them.

We have demonstrated, by acid-catalyzed transalkylation reactions and by GC-MS analysis of the products, that oxidative weathering reduces concentrations of several types of straight chain and branched chain aliphatic crosslinks. Infrared spectroscopic analysis shows that these crosslinks are converted to carbonyl and carboxyl groups. Plausible mechanisms for these transformations have been suggested.

INTRODUCTION

It is well known that oxidative weathering of coal induces irreversible structural changes that are detrimental to its utilization. For example, weathering decreases solvent extraction yields¹, coal liquefaction yield²⁻⁵ and hydrocarbon yield during pyrolysis⁶. It also reduces fluidity^{5,7,8} and calorific value⁹, and causes poor coking behavior^{10,11}. Irreversible changes in surface properties, that in turn affect coal beneficiation, also occur during weathering^{12,13}. Effects of oxidative weathering on coal properties have been recently reviewed by Berkowitz¹⁴ and by Gray and Lowenhaupt¹⁵.

Relatively little is known about the chemistry of coal weathering. It is known that the oxygen content of coal increases during weathering¹⁶. The changes in structural features due to weathering have mostly been monitored by infrared spectroscopy. Painter et al.¹⁷ and Fuller et al.¹⁸ observed an increase in the carbonyl absorption with a simultaneous decrease in the C-H absorption region during weathering at 398° K and above. However, Martin and Chao found that during the weathering of Argonne Premium coal samples (73.0-85.6% C, maf) under ambient conditions the carbonyl absorption increases while the C-H absorption

in the aliphatic region remains unaffected¹⁹. Liotta et al. found that the concentrations of ether and carboxylic acid groups increase upon prolonged ambient temperature weathering of Illinois #6 coal¹⁸. Painter et al. also have noted formation of carbonyl and carboxylic acid groups with concurrent decrease in aliphatic C-H intensity during the initial stages of air oxidation of a highly caking Pennsylvania coal¹⁷.

Our interest was to determine the fate of the aliphatic crosslinks during weathering. The aliphatic carbon structure, especially the crosslinks, play a significant role in coal liquefaction. The macromolecular network structure of bituminous and lower rank coals contains part of the aliphatic structure as methylene and polymethylene crosslinks connecting aromatic/hydroaromatic clusters. During liquefaction the relatively weak crosslinks undergo cleavage, while the hydroaromatic units provide part of the hydrogen for capping the free radicals produced by thermal decomposition¹. Therefore, the changes in aliphatic carbon distribution in coal during weathering can influence its liquefaction behavior.

There are as yet no accurate methods available for quantifying the aliphatic crosslinks in coal. Quantitative nature of the application of infrared (IR) spectroscopy is limited to certain general types of functional groups or bond types. Nuclear magnetic resonance spectroscopy, despite the success of dipolar dephasing techniques to decipher the extent of substitution on carbon atoms, is still inadequate to distinguish distinct structural entities^{20,21}.

In our studies, we have used acid-catalyzed transalkylation of coal using phenol and boron trifluoride, first reported by Heredy and Neuworth²², to quantify the aliphatic crosslinks in coals for monitoring changes in these crosslinks during weathering. It is assumed that during the transalkylation reaction, most of the methylene and polymethylene crosslinks are transferred to phenol. Since extensive solubilization is achieved by transalkylation, the information obtained from the analyses of the soluble products can provide useful information about coal structure. Although there are side reactions associated with the transalkylation reaction²³, we believe that it is adequate for comparing the relative features of raw and weathered coals. In addition to transalkylation, we have also used infrared studies to monitor the changes occurring during weathering.

EXPERIMENTAL

(a) Coal Samples. Three bituminous coals, namely, San Juan (New Mexico), Illinois #6, and Elkhorn (Kentucky) were used in the present study. Most of the studies were done on San Juan coal. The coals were collected from the freshly exposed mine faces. The samples were immediately transferred at the mine face to containers under a nitrogen atmosphere. The containers were closed tightly, sealed, and stored at approximately 273° K. The grinding and sieving were done under a nitrogen atmosphere. The ground and riffled samples were kept in glass jars, sealed under nitrogen, and stored in a refrigerator at 277° K. The proximate and ultimate analyses of the coal samples are given in Table 1.

(a) Weathering of Coal Samples. The coal samples, ground to -325 standard mesh, were subjected to accelerated weathering by heating them at 383° K in an air oven for 16 hours.

(c) Transalkylation. The procedure for transalkylation was essentially the same as that used by Heredy and Neuworth²². Briefly, coal (10 g) was slurried with phenol (100 g, Aldrich) in a three-necked round-bottomed flask equipped with a condenser and a thermometer, and heated to 373° K using a water bath. Boron trifluoride (Matheson) was bubbled through the coal-phenol slurry for 6 hours. The effluent gases were passed through saturated solution of sodium carbonate to neutralize the acids. At the end of 6 hours, BF₃ flow was stopped and the flask was purged with N₂ to remove any unreacted BF₃ and gaseous HF produced by the hydrolysis of BF₃. The reaction mixture, which now was a viscous suspension, was poured into 1 litre of ice-cold water. Sodium carbonate was added to the aqueous slurry with vigorous stirring until the aqueous layer was neutral. The neutralized reaction mixture was extracted successively with ether and toluene. Preliminary analyses by GC and HPLC indicated that the ether extract contained predominantly phenol and small quantities of coal-derived products. The toluene extract also contained phenol, but had a much larger proportion of coal-derived materials than the ether extract.

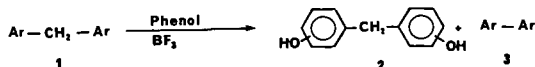
(d) Analyses of the Reaction Products. The ether and toluene extracts from the transalkylation reactions of fresh and weathered coals were analyzed by GC/MS on a VG-7070HS mass spectrometer in the EI mode. The mass spectrometer was interfaced with a Hewlett-Packard 5790 gas chromatograph. The GC column was a 35 meter long capillary with DB-1 as the stationary phase. A temperature program of 423-623° K at 8°/minute was used during the analysis. It was suspected that some of the high molecular weight phenolic compounds produced during the reaction may not be volatile enough for GC analysis. Therefore, the reaction mixture was silylated using N,O-bis trimethylsilylfluoroacetamide (BSTFA)²⁴ prior to analysis. Silylation of phenols converts them to silyl ethers, whose boiling points are considerably lower than those of the phenols. This procedure thus makes high molecular weight phenols more amenable to GC analysis. Bis-2 and bis-4 hydroxyphenyl methane were used as internal standards for quantification.

RESULTS AND DISCUSSION

Transalkylation involves the transfer of alkyl groups between aromatic nuclei, usually in the presence of strong Lewis acids. Heredy and Neuworth²² used this reaction to "depolymerize" coal. As a result of the reaction of coal with BF₃ and phenol, the solubility of coal in phenol or pyridine increased substantially. Various modifications of this reaction have since been reported²⁵⁻²⁸. Transalkylation reactions in the presence of trifluoromethane sulfonic acid and aromatic hydrocarbons have recently been used by Benjamin et al.²⁷ and Farcasiu et al.²⁸ to identify structural features in coals and heavy petroleum ends, respectively.

It is believed that during transalkylation the aliphatic side chains and crosslinks transfer from coal, without rearrangement, to the aromatic substrate such as phenol or toluene. A typical reaction is depicted in Scheme I.

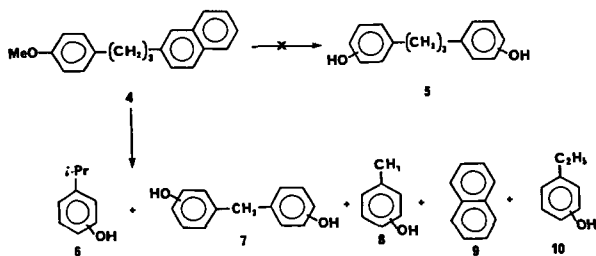
Scheme I. Transalkylation



For the above reaction to occur, the aromatic nuclei in compound 1 should carry activating groups, such as hydroxyl, alkoxy, or fused ring aromatics^{23,29}. As a result of reaction with BF_3 and phenol, the macromolecular structure of coal should undergo rupture at the aliphatic crosslinks, and these crosslinks are transferred to phenol molecules to produce bisphenols. Analysis of the bisphenols should provide information on the aliphatic crosslinks present in coal structure.

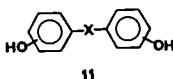
In model compounds, the aliphatic side chains on aromatic nuclei transalkylate without rearrangement^{30,31}. However, the reaction of aliphatic crosslinks is more complicated. For example, transalkylation of 1-(4-methoxyphenyl)-3-(2-naphthyl) propane (Compound 4) under BF_3 -phenol reaction conditions does not produce the expected 1,3-bishydroxyphenyl propane (Compound 5)²³. Instead, it gives a variety of products resulting from the rearrangement and fragmentation of the trimethylene crosslink in Compound 4, as shown in Scheme II.

Scheme II. Side Reactions During Transalkylation



Because of the above considerations, it is not possible to determine the exact nature and concentration of the crosslinks as they are present in coals by analysis of the transalkylation products. However, a comparison of the relative concentrations of the various crosslinks in different coal samples and how they change during weathering is possible. Specifically, our aim is to compare the relative concentrations of methylene and polymethylene crosslinks in fresh and weathered coals, so that the effect of weathering on these crosslinks can be assessed.

Numerous bisphenols of the general structure 11 were detected in both the ether and toluene extracts of the transalkylation products from the fresh and weathered coal samples.



X = straight or branched chain aliphatic crosslink

Table 2 contains a list of the aliphatic crosslinks detected in the toluene extract. Compounds with methylene crosslinks were predominant in the products from the fresh coal. This is consistent with the results of Benjamin et al.²⁷. It is interesting to note that several branched chain crosslinks appear in the transalkylation products from both the fresh and the weathered coals. Such crosslinks in coal structure have been reported only recently. Alkyl substituted methylene and ethylene crosslinks have been detected in a Wyodak coal by Benjamin et al.²⁷. In the present study, some of the branched chain crosslinks may have been formed by rearrangement of the straight chain crosslinks during transalkylation²³.

The relative concentrations of several types of hydrocarbon crosslinks, namely methylene(-CH₂-), ethylene(-CH₂-CH₂-), methyl methylene(-CH(CH₃)-), methyl ethylene(-CH(CH₃)-CH₂-), ethyl methylene(-CH(CH₂CH₃)-), and propyl methylene(-CH(CH₂CH₂CH₃)-) in the fresh and weathered San Juan coal are compared in Table 3. The concentrations are reported as a fraction of the toluene extract from the transalkylation reaction. As a result of weathering, concentrations of the most abundant, crosslinks namely, methylene, ethylene, methyl methylene, and ethyl methylene groups are reduced by factors of 6, 14, 6, and 9 respectively. The differences in the concentrations of larger crosslinks were not measured because of their low abundance in the transalkylated products.

The results in Table 3 clearly indicate that the aliphatic crosslinks have been altered significantly by oxidative weathering. The question is: what are these crosslinks converted to? Liotta et al. have detected, by infrared analysis, increases in carboxylic acid groups and ether linkages after long term ambient temperature weathering of an Illinois #6 coal¹⁸. Painter et al. have obtained infrared spectroscopic evidence for a decrease in the aliphatic stretching intensity (2900 cm⁻¹ region) and an increase in the carbonyl stretching (1700-1765 cm⁻¹ region) after weathering of a highly caking Pennsylvania coal^{17,32}. They speculate the formation of ester groups, in addition to ketones and carboxyl groups, as a result of extended weathering at about 373° K. Jakab et al. have reported that weathering of subbituminous coals causes changes in both the aliphatic and aromatic structures of coal³³. They detected, by Curie Point pyrolysis GC-MS, an increase in carbonyl groups in the coals weathered in air at 373° K. In addition, they found decreased yields of alkylnaphthalenes and phenols from the weathered coal compared to the fresh coal. The decrease was attributed to condensation reactions involving alkyl aromatics and phenolic

fragments resulting in large clusters. Gethner has speculated that formation of ketones, aldehydes, esters, and ethers is likely during oxidative weathering of coals at 373° K³⁴. Recently, Fuller has obtained high temperature infrared spectroscopic data which indicate that during oxidative weathering at 473° K or above¹⁸, several surface groups such as ketones, aldehydes, carboxylic acids, and anhydrides of carboxylic acids are formed.

We have examined the infrared spectra of three coals before and after overnight weathering in air at 383° K. The infrared spectra of the fresh coals, their corresponding weathered samples, and the difference spectra between the weathered and fresh coals are given in Figures 1-3. Several changes due to weathering are observed. The most significant changes are the enhanced carbonyl absorptions in the 1700 cm⁻¹ region, and decreases in the aliphatic C-H absorptions in the 2850-2950 cm⁻¹ (CH stretching) and 1450 cm⁻¹ (CH₂ bending) regions. These changes are quite discernible in the difference spectra. Minor changes are observed in the aromatic CH vibrations in the 750 - 850 cm⁻¹ region as well, especially in the Elkhorn coal.

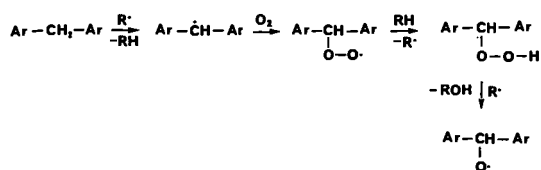
With regard to the results of our infrared study, a word of caution is appropriate. The large decreases in the concentration of the aliphatic crosslinks after weathering, as measured by transalkylation (Table 3), cannot be expected to match those indicated in the difference infrared spectra between weathered and fresh coals. This is because the spectra measure the total aliphatic content of the samples, namely aliphatic crosslinks, hydroaromatics, and aliphatic side chains. In contrast, results in Table 2 show differences in relative concentrations of the aliphatic crosslinks, which represent only a small part of the total aliphatics. Furthermore, concentrations measured by transalkylation correspond to only the soluble fractions of the reaction products; some of the more complex transalkylation products may be retained in the residue itself.

Our transalkylation studies show that the concentrations of methylene and other aliphatic crosslinks decrease during oxidative weathering. The infrared analysis shows that carbonyl groups are produced during weathering. Therefore, it is quite likely that during our weathering conditions the aliphatic crosslinks are oxidized to carbonyls and/or carboxylic acid groups.

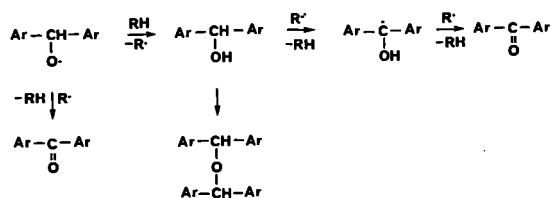
A possible mechanism of oxidation of methylene groups to carbonyl groups involves autooxidation (oxidation by molecular oxygen) at the benzylic position. Autooxidation of arylalkanes is a facile reaction with low activation energies; for example, 6.0 kcal/mole for 1,1-diphenylethane and, 13.3 kcal/mole for toluene^{35,38}.

Autooxidation of coals can be initiated by abstraction of a benzylic hydrogen atom by free radicals already present in coals³⁷⁻³⁹. The resulting benzylic radical then reacts with oxygen to form a peroxy radical, which abstracts a H-atom from elsewhere in the coal "molecule" to form a hydroperoxide. Formation of hydroperoxide during weathering is speculated by other workers as well^{16,40,41}. The hydroperoxide can undergo homolysis at the peroxy bond (activation energy = 35 kcal/mole) to generate an alkoxy radical (Scheme III) which can undergo various reactions to produce carbonyl compounds. Some of the possible reactions of the alkoxy radical are represented in Schemes IV and V.

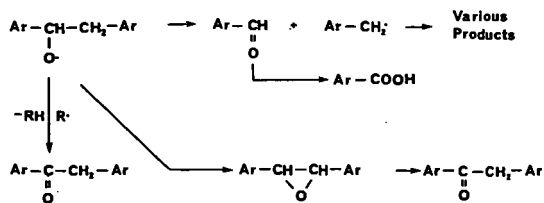
Scheme III. Possible Oxidation Pathways



Scheme IV. Possible Oxidation Pathways(contd.)



Scheme V. Possible Oxidation Pathways(contd.)



There is ample evidence in the literature for conversion of reactive hydrocarbons to carbonyl compounds by autooxidation⁴²⁻⁴⁸. In coals, the final products of autooxidation under the conditions used in the present study could be a mixture of carbonyl and carboxylic acid surface groups. Under mild oxidation conditions, a different set of functional groups such as ethers as proposed by Liotta et al.¹⁶ or epoxides as suggested in Scheme V could be formed. There are numerous examples of alkoxy radicals rearranging to epoxides⁴⁹⁻⁵¹. Choi and Stock have shown that ethers can be produced from benzhydrol structures, which are invoked as intermediates in Scheme IV⁵². At higher temperatures, the epoxides and ethers are unstable and may rearrange to carbonyl compounds.

CONCLUSIONS

Oxidative weathering of coal causes a significant decrease in the concentration of aliphatic crosslinks; the relative decrease was determined by acid-catalyzed transalkylation of coal with phenol. Infrared analysis of the raw and weathered coals indicate that the hydrocarbon crosslinks are converted to carbonyl groups. Plausible explanations have been offered for the formation of carbonyl groups from aliphatic crosslinks.

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TABLE I. Proximate and Ultimate Analyses of Coals

| | <u>San Juan</u> | <u>Ill #6</u> | <u>Elkhorn</u> |
|---|-----------------|---------------|----------------|
| <u>Proximate Analysis (wt %, dry basis)</u> | | | |
| Ash | 11.4 | 11.8 | 6.6 |
| Volatile Matter | 44.2 | 39.7 | 38.7 |
| Fixed Carbon | 44.4 | 48.5 | 54.8 |
| <u>Ultimate Analysis (wt %, dmmf*)</u> | | | |
| Carbon | 78.9 | 78.9 | 85.4 |
| Hydrogen | 6.0 | 5.4 | 5.7 |
| Nitrogen | 1.6 | 1.2 | 1.8 |
| Chlorine | 0.1 | 0.1 | 0.2 |
| Sulfur | 1.0 | 4.4 | 0.7 |
| Oxygen (by diff.) | 12.4 | 10.0 | 6.3 |

*Dry, mineral matter-free basis

TABLE II. Crosslinks Detected in the Transalkylated Products

| <u>Crosslink</u> | <u>Formula</u> |
|------------------|--|
| Methylene | -CH ₂ - |
| Ethylene | -CH ₂ -CH ₂ - |
| Methylmethylene | -CH(CH ₃)- |
| Ethylmethylene | -CH(CH ₂ CH ₃)- |
| Propyl methylene | -CH(CH ₂ CH ₂ CH ₃)- |
| Methylethylene | -CH(CH ₃)-CH ₂ - |
| Ethylethylene | -CH(CH ₂ CH ₃)-CH ₂ - |
| Butylmethylene | -CH(CH ₂ CH ₂ CH ₂ CH ₃)- |

TABLE III. Relative Concentrations of Crosslinks in the Transalkylated Products from Fresh and Weathered San Juan Coal.

| <u>Crosslink</u> | <u>Relative Concentration</u> | | <u>Ratio: Fresh/Weathered</u> |
|---|-------------------------------|------------------|-----------------------------------|
| | <u>Fresh</u> | <u>Weathered</u> | |
| -CH ₂ - | 5.16 | 0.85 | 6 |
| -CH ₂ -CH ₂ - | 1.8 | 0.13 | 14 |
| -CH(CH ₃)- | 1.08 | 0.17 | 6 |
| -CH(CH ₃)-CH ₂ - | 1.04 | 0.11 | 9 |
| -CH(CH ₂ CH ₃)- | 0.67 | 0.09 | 7 |

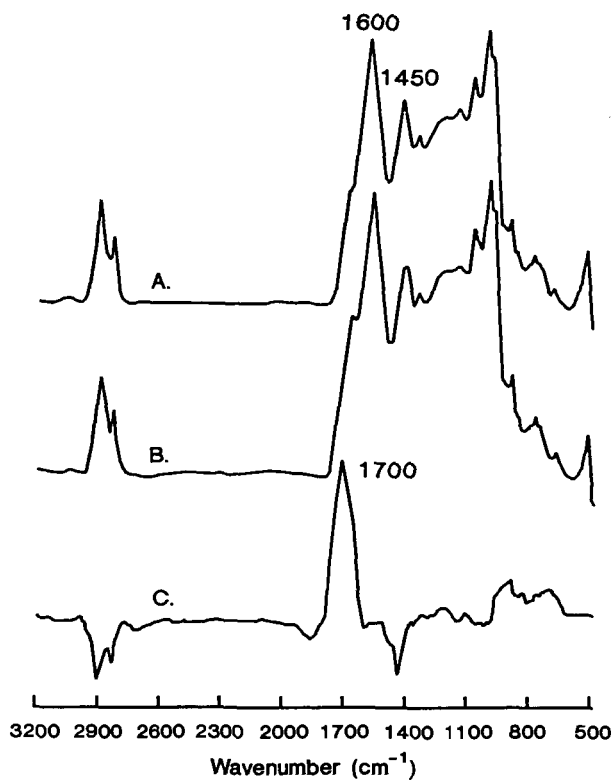


Figure 1. Infrared spectra of San Juan coal
A. Fresh coal, B. Weathered coal, and C. Difference
spectrum (B-A).

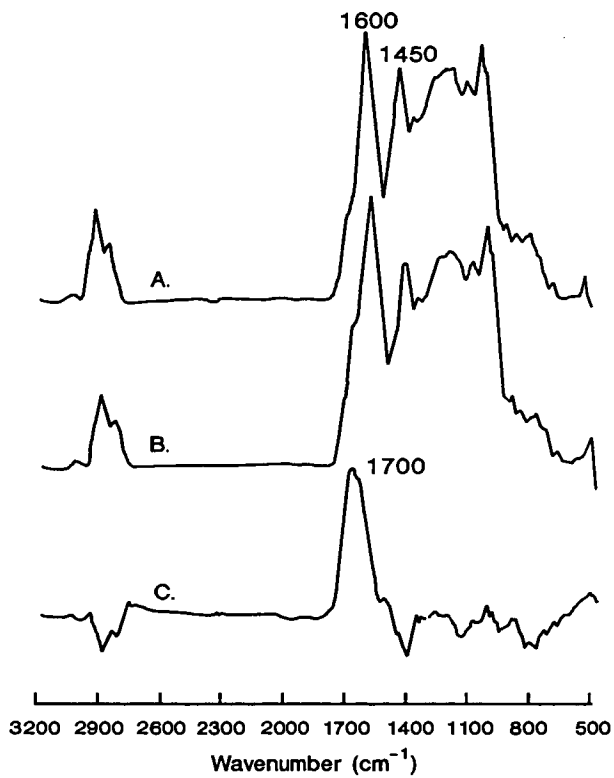


Figure 2. Infrared spectra of Illinois #6 coal
A. Fresh coal, B. Weathered coal, and C. Difference spectrum (B-A).

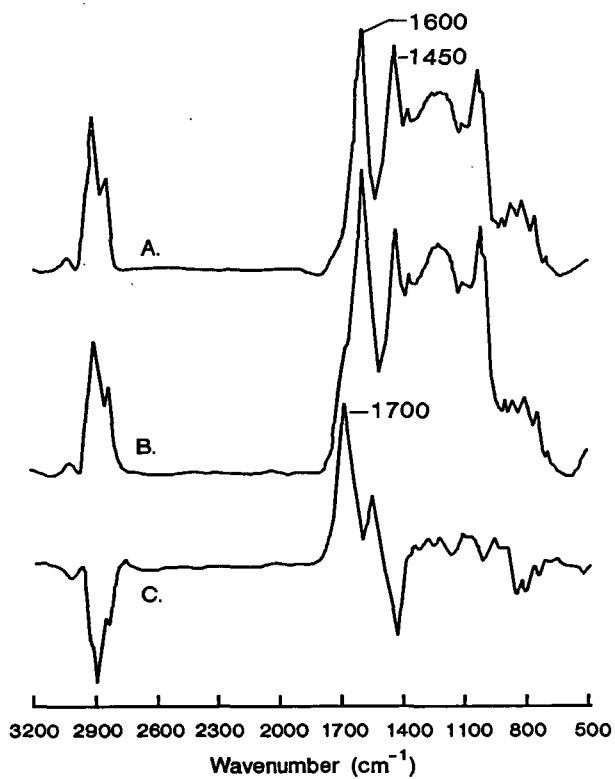


Figure 3. Infrared spectra of Elkhorn coal
A. Fresh coal, B. Weathered coal, and C. Difference spectrum (B-A).